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PHOSPHORIC ACID, META

[37267-86-0]

Formula HPO_3 ; MW 79.98; the general formula $(\text{HPO}_3)_n$; in vapor phase it probably exists as monomeric HPO_3

Synonyms: metaphosphoric acid; glacial phosphoric acid. Long chain linear or cyclic metaphosphoric acids of formula $(\text{HPO}_3)_n$ are also called poly-metaphosphoric acids.

Uses

Metaphosphoric acid is used in making oxyphosphate dental cement. It also is used as an analytical reagent.

Physical Properties

Glass-like colorless solid; soft and transparent; deliquesces; density 2.2 to 2.5 g/cm³; sublimes at red heat; dissolves slowly in cold water, decomposing to phosphoric acid; soluble in alcohol.

Thermochemical Properties

$$\Delta H_f^\circ \quad -226.7 \text{ kcal/mol}$$

Preparation

Metaphosphoric acid is obtained as a polymeric glassy solid by prolonged heating of phosphoric acid. Either phosphoric acid, H_3PO_4 , or pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, when heated above 300°C, on cooling yields the transparent glassy mass of composition $(\text{HPO}_3)_n$.

Metaphosphoric acid also is obtained from partial hydration of phosphorus pentoxide by dissolving it in cold water.

Analysis

Elemental composition: P 38.73%, H 1.26%, O 60.01%. The compound may be identified by physical properties alone. It may be distinguished from ortho and pyrophosphates by its reaction with a neutral silver nitrate solution. Metaphosphate forms a white crystalline precipitate with AgNO_3 , while PO_4^{3-} produces a yellow precipitate and $\text{P}_2\text{O}_7^{3-}$ yields a white gelatinous precipitate. Alternatively, metaphosphate solution acidified with acetic acid forms a white precipitate when treated with a solution of albumen. The other two phosphate ions do not respond to this test. A cold dilute aqueous solution may be analyzed for HPO_3^- by ion chromatography using a styrene divinylbenzene-based low-capacity anion-exchange resin.

PHOSPHORIC ACID, ORTHO

[7664-38-2]

Formula H_3PO_4 ; MW 97.995; also forms a hemihydrate $\text{H}_3\text{PO}_4 \cdot 1/2 \text{H}_2\text{O}$ [16271-20-8], known as diphosphoric acid; crystals of anhydrous acid or hemi-

hydrate consist of tetrahedral PO_4 units linked by hydrogen bonding.

Structure $(\text{OH})_3\text{P}=\text{O}$.

Synonyms: phosphoric acid; trihydrogen phosphate.

History and Uses

Phosphoric acid was prepared first by Robert Boyle in 1694 by dissolving phosphorus pentoxide in water. Phosphoric acid is probably the most important compound of phosphorus. It is the second largest inorganic chemical by volume, after sulfuric acid, marketed in the United States. The single most important application of this acid is manufacturing phosphate salts for fertilizers. Such fertilizer phosphates include sodium, calcium, ammonium, and potassium phosphates. Other applications are in metal pickling and surface treatment for removal of metal oxides from metal surfaces; electropolishing of aluminum; as a bonding agent in various refractory products such as alumina and magnesia; as a catalyst in making nylon and gasoline; as a dehydrating agent; in fireproofing wood and fabrics; in lithographic engraving; in textile dyeing; in dental cement; in coagulating rubber latex; in purifying hydrogen peroxide; and as a laboratory reagent. Dilute solutions of phosphoric acid are used as additives to carbonated beverages for a pleasing sour taste. Also, dilute acid is used in refining sugar; as a nutrient; and as a buffering agent in preparing jam, jelly, and antibiotics. The commercial phosphoric acid is 85% (w/w) in strength.

Physical Properties

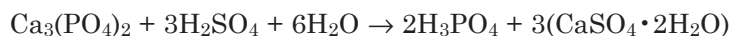
White orthorhombic crystals in pure and anhydrous state or a clear, syrupy liquid; melts at 42.35°C ; hygroscopic; can be supercooled into a glass-like solid; crystallizes to hemihydrate, $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$ on prolonged cooling of 88% solution; hemihydrate melts at 29.32°C and loses water at 150°C ; density 1.834 g/cm^3 at 18°C ; density of commercial H_3PO_4 (85%) 1.685 g/mL at 25°C ; pH of 0.1N aqueous solution 1.5; extremely soluble in water, 548 g/100mL at room temperature; soluble in alcohol.

Thermochemical Properties

ΔH_f°	-305.7 kcal/mol
ΔG_f°	-243.5 kcal/mol
S°	26.41 cal/deg mol
C_p	25.35 cal/ degree mol
ΔH_{soln}	2.79 kcal/mol

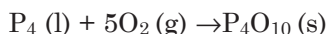
Production

Low-purity technical grade phosphoric acid for use in fertilizers is produced from phosphate rocks by digestion with concentrated sulfuric acid. The apatite types, primarily consisting of calcium phosphate phosphate rocks, are used:



The insoluble calcium sulfate slurry is filtered out. Acid from this wet process is impure but can be purified by various methods. Purification steps involve precipitation, solvent extraction, crystallization, and ion exchange techniques.

Phosphoric acid also can be made by many different methods. Dissolution of phosphorus pentoxide in water and boiling yields phosphoric acid. Pure phosphoric acid can be obtained by burning phosphorus in a mixture of air and steam:



The acid also may be prepared by heating violet phosphorus with 33% nitric acid:



or by heating red phosphorus with nitric acid (1:1). The overall equation is:

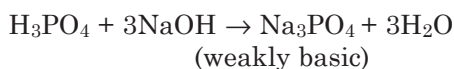
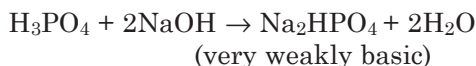
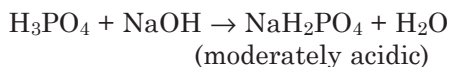


Reactions

Phosphoric acid is a tribasic acid. It is not an oxidizing acid. In aqueous solution phosphoric acid dissociates to H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} ions. The dissociation constants are as follows:



Thus, out of the three ionizable hydrogens in phosphoric acid, the first H^+ is removed more easily than the second, and the second H^+ dissociates more easily than the third. When phosphoric acid is titrated with sodium hydroxide, it forms both acidic and basic salts:



At first, the pH of the solution suddenly changes to 4.5 upon completing formation of NaH_2PO_4 , and there is a second change of pH to around 9.0 after Na_2HPO_4 is formed completely. The titration curve for $\text{H}_3\text{PO}_4=\text{NaOH}$ shows two pH inflection points. Mixtures of Na_2HPO_4 and NaH_2PO_4 , therefore, exhibit buffer properties at pH 6 to 8. Because of a big difference in the first two ionization constants, phosphoric acid can be titrated as a monobasic or a dibasic acid. Aqueous solution of trisodium phosphate, Na_3PO_4 is basic.

Heating phosphoric acid converts it to metaphosphoric acid, HPO_3 , and pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$. If anhydrous phosphoric acid is melted and allowed to stand for several weeks, it partially converts to pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$. The equilibrium occurs in liquid phase:

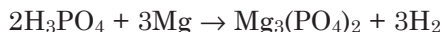


However, when heated at 215°C , it is fully converted to pyrophosphoric acid.

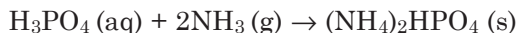
When heated at 300° , phosphoric acid converts to metaphosphoric acid, HPO_3 :



Phosphoric acid reacts with most metals and their oxides at temperatures above 400°C forming metal phosphates. Reactive metals, such as magnesium, react with phosphoric acid solutions forming magnesium phosphate and evolving hydrogen:



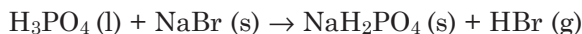
When ammonia gas is bubbled through phosphoric acid solution, diammonium hydrogen phosphate is produced:



Reaction with calcium triphosphate fluoride yields calcium dihydrogen phosphate, a component of superphosphate fertilizer:



When heated with solid sodium bromide, phosphoric acid yields sodium dihydrogen phosphate, liberating hydrogen bromide:



Analysis

The orthophosphate anion, PO_4^{3-} can be analyzed readily in aqueous solution by either ion chromatography or colorimetry. The aqueous solution must be diluted for such analyses. In colorimetric measurement, the solution is treated with a reagent mixture containing ammonium molybdate and ammo-

mium metavanadate under acid conditions to form the yellow color of vanadomolybdophosphoric acid. The yellow absorbance or transmittance may be measured at λ 470nm. Alternatively, the solution after treatment with ammonium molybdate may be reduced by stannous chloride to produce an intense blue color of molybdenum blue which may be measured at λ 650 nm. The concentration of PO_4^{3-} may be calculated from a standard calibration curve. The normality of phosphoric acid can be measured by titration with a standard solution of NaOH using a suitable color indicators or a pH meter.

PHOSPHORIC ACID, PYRO

[2466-09-3]

Formula: $\text{H}_4\text{P}_2\text{O}_7$; MW 177.98

Structure: $(\text{HO})_2\text{P}(=\text{O})\text{—O—P}(=\text{O})(\text{OH})_2$

Synonym: disphosphoric acid

Uses

No commercial application of this acid is known. The pyrophosphate salts usually are not made from the acid.

Physical Properties

Colorless needles or liquid; hygroscopic. Crystallizes in two anhydrous forms: a metastable form melting at 54.3°C and a second and more stable form melting at 71.5°C ; extremely soluble in cold water, reacting very slowly to form phosphoric acid; decomposing much faster in hot water; very soluble in alcohol and ether.

Preparation

Pyrophosphoric acid may be prepared by heating orthophosphoric acid at 215°C :

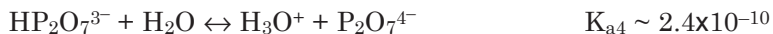


The acid solution in pure form can be obtained by ion exchange, passing an aqueous solution of sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, through a suitable cation exchange column.

Reactions

The acid has four replacable H^+ ions. Its dissociation constants indicate that two H^+ ions are strongly acidic while the other two protons are weakly acidic. The first dissociation constant especially is very large:





Pyrophosphoric acid forms acid salts, such as $\text{NaH}_3\text{P}_2\text{O}_7$ and $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$.

Analysis

Pyrophosphoric acid may be converted into its acid salts which may be characterized individually by physical and x-ray properties and elemental compositions.

PHOSPHORUS

[7723-14-0]

Symbol P; atomic number 15; atomic weight 30.974; a Group VA (Group 15) nonmetallic element of nitrogen group; electron configuration $[\text{Ne}]3s^23p^3$; valence states -3, +3, +5; most stable valence state +3; atomic radius 1.10Å; one natural isotope P-31 (100%); nine radioactive isotopes in the mass range 26, 28–30, 32–36; the longest-lived radioisotopes P-33, $t_{1/2}$ 25.3 day

History, Occurrence, and Uses

Elemental phosphorus was discovered in 1669 by Hennig Brand. About two hundred years later James Readman developed a process for phosphorus recovery from phosphatic rocks using an electric furnace.

Phosphorus is one of the most widely distributed elements on earth. It is found as phosphate salts in nearly all igneous rocks and in sedimentary deposits and sea beds. Phosphorus occurs in more than three hundred minerals, usually associated with Ca, Mg, Fe, Sr, Al, Na, and several other metals, and with anions such as silicates, sulfates, oxides, hydroxides, and halides.

Phosphorus is an essential element present in all living matter and is vital in biological and ecological processes. It occurs in DNA and other nucleic acids, and in bones.

Phosphorus is used in pyrotechnics, smoke bombs, incendiary shells, and safety matches. It also is used in organic syntheses, manufacture of phosphoric acid, phosphorus trichloride, phosphine, and other compounds.

Physical Properties

Elemental phosphorus in solid phase exists in three major allotropic forms: (1) white or yellow phosphorus that may occur in alpha or beta modification, (2) red phosphorus, and (3) black phosphorus.

White phosphorus is a white, soft, wax-like transparent mass which often acquires a yellow appearance due to impurities, especially traces of red phosphorus. It has a garlic-like odor. It is made up of cubic crystals, has a density 1.82 g/cm³, and melts at 44.1°C to a colorless or yellowish liquid. X-ray diffraction studies and ³¹P-NMR analysis indicate tetrahedral P₄ molecules with an interatomic distance of 2.21Å, and the molecules are able to rotate freely

in the crystals. When cooled below -76.9°C , the cubic alpha form converts to a hexagonal beta modification with a density 1.88 g/cm^3 . The beta form, unlike the alpha form, does not rotate freely in the crystal but has a fixed orientation of P_4 molecules in the lattice.

Red phosphorus is obtained from white phosphorus by heating at 230 to 240°C , allowing complete conversion to occur in about 48 hours. Conversion is catalyzed by sulfur, iodine, and selenium. The red allotrope also slowly deposits from liquid phosphorus or from a solution of white phosphorus, the rate and yield depending on catalysts, temperature, light, and other factors. Red phosphorus exhibits various modifications. Three important ones are an amorphous form at ordinary temperatures and two crystalline modifications which include a triclinic form and a hexagonal or a tetragonal form that may prevail at higher temperatures. There also are a few more modifications, all of which may coexist, accounting for variability in physical properties of red phosphorus. The triclinic variety of red phosphorus is the most stable of all allotropes of phosphorus at ordinary temperatures. Red phosphorus possesses a density of 2.0 to 2.31 g/cm^3 and melts at 590°C .

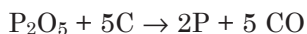
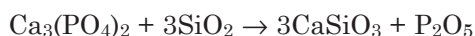
Black phosphorus is the third major allotropic form of phosphorus. It occurs in two forms, one is an amorphous modification having a laminar structure similar to graphite and the other is an orthorhombic crystalline form. The density of black phosphorus may vary between 2.20 to 2.69 g/cm^3 . Black phosphorus is obtained from white phosphorus by heating the latter at 220°C under an extremely high pressure of about $10,000\text{ atm}$.

When solid phosphorus of any form—white, red, or black—is melted, it forms the same liquid phosphorus. This liquid has a density of 1.74 g/cm^3 and viscosity 1.69 centipoise at 50°C . Liquid phosphorus boils at 280.5°C . Upon cooling, liquid phosphorus solidifies to only white phosphorus. Liquid phosphorus and its vapors consist of tetrahedral P_4 molecules. The vapors, on rapid condensation, convert to white phosphorus.

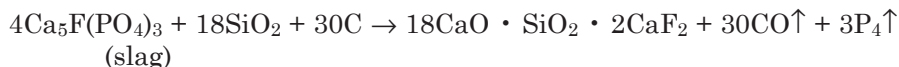
While white and red phosphorus have high electrical resistivity, the black variety has a low resistivity of 0.71 ohm-cm at 0°C . Solubility also varies widely. White phosphorus is soluble in a number of organic solvents. It is very highly soluble in carbon disulfide, about $400\text{ g/100 g solvent}$ at 0°C and moderately soluble in benzene ($\sim 3.59\text{ g/100g}$ at 25°C) and exhibits lower solubility in ether ($\sim 1.5\text{g/100g}$ at 25°C). Red and black phosphorus are insoluble in organic solvents. White phosphorus is a flammable solid, igniting spontaneously in air at 35°C . Red and black phosphorus are nonflammable. The latter is difficult to ignite.

Production

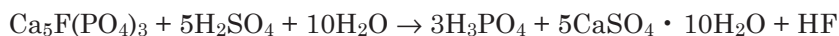
White phosphorus usually is obtained by heating some form of calcium phosphate with quartz and coke, usually in an electric furnace. The reactions may be written in two steps as follows:



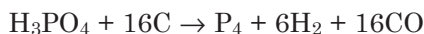
In commercial scale, white phosphorus is manufactured mostly from the mineral fluorapatite by heating with silica and coke in an electric-arc or blast furnace at a temperature of 1,200 to 1,500°C. An overall reaction may be represented in the following equation.



White phosphorus also can be produced by a wet process using phosphoric acid, a process that was practiced historically in commercial production. In this method the starting material, phosphoric acid, usually is prepared in large vats by reacting phosphate rock with sulfuric acid:



Phosphoric acid is filtered out of the mixture. It is then mixed with coke, charcoal or sawdust; dried; charred; and finally heated to white heat in a fire-clay retort:



The vapor is condensed to obtain white phosphorus.

As stated earlier, all other forms of phosphorus can be made from white phosphorus. Thus, heating white phosphorus first at 260°C for a few hours and then at 350°C gives red phosphorus. The conversion is exothermic and can become explosive in the presence of iodine as a catalyst. When a solution of white phosphorus in carbon disulfide or phosphorus tribromide is irradiated the scarlet red variety is obtained.

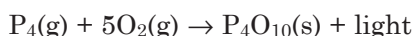
Black phosphorus allotrope is produced by heating white phosphorus at 220°C under 12,000 atm pressure. The conversion is initially slow, but can become fast and explosive after an induction period.

White phosphorus is stored under water as it ignites in air. It may be cut into appropriate sizes only under water.

Reactions

Reactivity of white phosphorus is much greater than red or black phosphorus. Black phosphorus is the least reactive of all phosphorus allotropes.

White phosphorus ignites in air spontaneously. When placed on a paper, the paper catches fire after a short delay. It catches fire at about 35°C. At room temperature white phosphorus glows in the dark on exposure to air emitting faint green light. Such chemiluminescence is attributed to the oxidation of P_4 molecules in the vapor phase in contact with the surface of solid phosphorus:

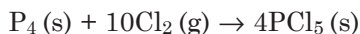
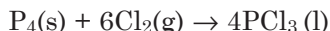


The mechanism involves a complicated oxidative process that occurs only at

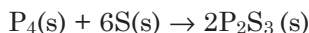
certain partial pressures of oxygen and not in pure oxygen at atmospheric pressure, nor in vacuum.

Red phosphorus ignites when struck with a hammer blow or when heated at 260°C. Black phosphorus ignites in contact with flame.

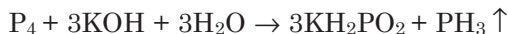
White phosphorus reacts spontaneously with halogens at ordinary temperatures forming phosphorus trihalides. However, in excess halogen the product is phosphorus pentahalide:



White phosphorus reacts with sulfur on warming forming phosphorus trisulfide:

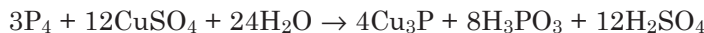
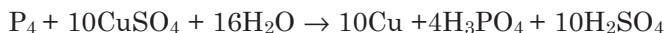


White phosphorus reacts with strong aqueous alkali solution forming hypophosphite with evolution of phosphine, PH_3 :



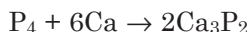
Strong oxidizing agents, such as nitric acid (cold and concentrated), oxidize phosphorus to phosphoric acid.

Reaction with copper sulfate solution forms a mixture of metallic copper and copper(I) phosphide. The two reactions may be written separately as follows:



Similar reactions occur with the salts of other easily reducible metals, such as silver and gold, in aqueous salt solutions.

Phosphorus combines with several metals on heating, forming their phosphides.



Reactions with alkali metals occur under warm conditions producing the corresponding metal phosphides:



Analysis

The allotropes of phosphorus may be identified from their physical properties. White phosphorus can be identified from its chemiluminescence (a pale

green glow) at a specific range of oxygen partial pressure at room temperature. Furthermore, it spontaneously ignites in air at 35°C. It also imparts chemiluminescence to water when boiled. Elemental phosphorus can be analyzed by GC/MS. Its solution in a suitable organic solvent, such as benzene may be injected, onto the GC and identified from the mass spectra. In solution it exists as P_4 molecule, thus the characteristic molecular ion should have the mass 124. Red phosphorus can be converted into its white allotrope by heating in the absence of air to above 260°C and condensing the vapors and trapping in an organic solvent for analysis by GC/MS.

Hazards

White phosphorus is a highly toxic substance, both an acute and chronic toxicant. Chronic exposure to its vapors can cause "phossy jaw," necrosis of the jaw. Other symptoms are bronchopneumonia, bone changes, anemia and weight loss. Ingestion can cause nausea, vomiting, abdominal pain, diarrhea and coma. Skin contact can cause severe burns. In the eye it damages vision. Red phosphorus is much less toxic than its white allotrope. Its fumes, when burned, are highly irritating. White phosphorus is a flammable solid, igniting spontaneously when exposed to air.

PHOSPHORUS ACID

[13598-36-2]

Formula: H_3PO_3 ; MW 82.00; a dibasic acid

Structure: $HP(=O)(OH)_2$

Synonym: orthophosphorus acid

Uses

Phosphorus acid is used to prepare phosphite salts. It is usually sold as a 20% aqueous solution.

Physical Properties

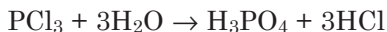
White crystalline mass; deliquescent; garlic-like odor; density 1.651 g/cm³ at 21°C; melts at 73.6°C; decomposes at 200°C to phosphine and phosphoric acid; soluble in water, about 310 g/100mL; K_1 5.1×10^{-2} and K_2 1.8×10^{-7} ; soluble in alcohol.

Thermochemical Properties

$$\Delta H_f^\circ \quad -230.5 \text{ kcal/mol}$$

Preparation

Phosphorus acid can be prepared by the reaction of phosphorus trichloride with water:



The reaction is violent. Addition of PCl_3 should be extremely cautious and slow. The addition can be carried out safely in the presence of concentrated HCl . Alternatively, a stream of air containing PCl_3 vapor is passed into ice-cold water and solid crystals of H_3PO_4 form.

Alternatively, phosphorus acid can be prepared by adding phosphorus trichloride to anhydrous oxalic acid:



In this reaction, all products except H_3PO_3 escape as gases leaving the liquid acid.

Dissolution of phosphorus sesquioxide in water also forms phosphorus acid. When shaken with ice water, phosphorus acid is the only product .



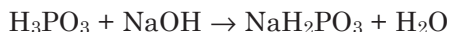
However, in hot water part of the phosphorus acid disproportionates to phosphoric acid and phosphorus or phosphine.

Reactions

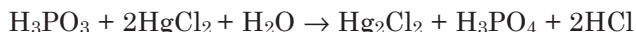
Phosphorus acid on heating at 200°C converts to phosphoric acid and phosphine:



Phosphorus acid is a moderately strong dibasic acid. It reacts with alkalis forming acid phosphites and normal phosphites. Thus, reaction with sodium hydroxide gives sodium dihydrogen phosphite and disodium hydrogen phosphite, but not sodium phosphate, Na_3PO_4 .



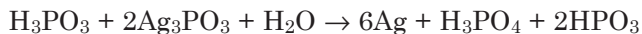
Phosphorus acid is a powerful reducing agent. When treated with a cold solution of mercuric chloride, a white precipitate of mercurous chloride forms:



Mercurous chloride is reduced further by phosphorus acid to mercury on heating or on standing:



Phosphorus acid reacts with silver nitrate in dilute solution yielding a white precipitate of silver phosphite, Ag_3PO_3 , which reduces to metallic silver.



Analysis

Elemental composition: P 37.78%, H 3.69%, O 58.54%. The acid in solid form may be identified by its physical properties. Aqueous solution may be heated and phosphorus acid is converted to phosphoric acid which is measured for orthophosphate ion by ion chromatography or colorimetry (see Phosphoric Acid). A cold aqueous solution may be analyzed for phosphite ion by ion chromatography, following appropriate dilution. Strength of the acid in an aqueous solution may be measured by acid-base titration using a standard solution of alkali. Also, titration against a standard solution of silver nitrate using potassium chromate as indicator may serve as an additional confirmatory test.

PHOSPHORUS OXYCHLORIDE

[100025-87-3]

Formula: POCl_3 ; MW 153.33

Synonym: phosphoryl chloride

Uses

Phosphorus oxychloride is a chlorinating agent in many organic preparative reactions. It also is a solvent in cryoscopy.

Physical Properties

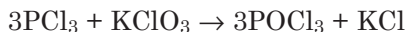
Colorless fuming liquid with a pungent odor; density 1.645 g/mL; freezes at 1°C; boils at 105.5°C; reacts with water and ethanol.

Thermochemical Properties

ΔH_f° (liq)	-142.7 kcal/mol
ΔH_f° (gas)	-133.5 kcal/mol
ΔG_f° (liq)	124.5 kcal/mol
ΔG_f° (gas)	-122.6 kcal/mol
S° (liq)	53.2 cal/deg mol
S° (gas)	77.8 cal/deg mol
C_p (liq)	33.2 cal/deg mol
C_p (gas)	20.3 cal/deg mol
ΔH_{fus}	3.13 kcal/mol
ΔH_{vap}	8.21 kcal/mol

Preparation

Phosphorus oxychloride can be prepared from phosphorus trichloride or phosphorus pentachloride. It can be obtained from phosphorus trichloride by cautious addition of potassium chlorate:



The oxychloride also is obtained by the action of boric acid or oxalic acid with phosphorus pentachloride:



Phosphorus oxychloride also is made by heating calcium phosphate in a current of chlorine and carbon monoxide at 350°C:



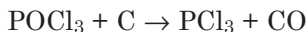
Alternatively, heating a mixture of calcium phosphate and carbon in a current of chlorine at 750°C yields the oxychloride.

Reactions

Phosphorus oxychloride hydrolyzes in water forming phosphoric acid:



When the vapors of phosphorus oxychloride are passed over carbon at red heat, phosphorus trichloride is produced:



The oxychloride also is reduced by hydrogen, carbon monoxide and other reducing agents.

Analysis

Elemental composition: P 20.20%, O 10.43%, Cl 69.36%. The compound is hydrolyzed in water and the products phosphoric and hydrochloric acids are measured by a colorimetric method for orthophosphate ion (see Phosphoric Acid, Analysis), and titration with silver nitrate for the chloride ion. Also, phosphate and chloride ions can be measured by ion chromatography.

Toxicity

The compound is highly irritating to skin, eyes and mucous membranes. Inhaling its vapors can cause pulmonary edema.

PHOSPHORUS PENTACHLORIDE

[10026-13-8]

Formula: PCl_5 ; MW 208.24

Uses

Phosphorus pentachloride is used as a chlorinating agent in many organic syntheses, such as production of alkyl and acid chlorides. It also is a catalyst in manufacturing acetylcellulose.

Physical Properties

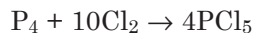
Yellowish-white tetragonal crystals; pungent odor; fumes in air; deliquescent; density 2.1 g/cm³; decomposes on heating; melts at 166.8°C under the pressure of its own vapor(triple point); sublimes at 160°C; critical temperature 373°C; hydrolyzes in water; soluble in carbon disulfide and carbon tetrachloride.

Thermochemical Properties

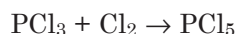
$$\Delta H_f^\circ \quad -106 \text{ kcal/mol}$$

Preparation

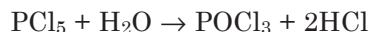
Phosphorus pentachloride is prepared by reacting white phosphorus with excess dry chlorine. The white phosphorus is placed over sand in a retort from which air and moisture have been purged. The reaction is indicated by flaming phosphorus:



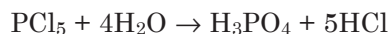
Also, the compound is obtained by reaction of dry chlorine with phosphorus trichloride:

**Reactions**

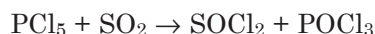
Phosphorus pentachloride absorbs moisture from air forming phosphoryl chloride:



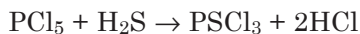
The above reaction is difficult to control and progresses to complete hydrolysis. Thus, in the presence of excess water or when treated with water, the pentachloride is hydrolyzed to phosphoric acid:



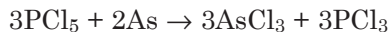
Reaction with sulfur dioxide yields thionyl chloride and phosphoryl chloride:



Reaction with liquid hydrogen sulfide forms thiophosphoryl chloride, PSCl_3 :



Phosphorus pentachloride converts arsenic to arsenic trichloride:



Reaction with oxalic acid or boric acid yields phosphoryl chloride:



Reaction with phosphorus pentoxide produces phosphoryl chloride:



Analysis

Elemental composition: P 14.88%, Cl 85.12%. The compound may be hydrolyzed with water and the products phosphoric and hydrochloric acids are measured for phosphate and chloride ions by ion chromatography and colorimetric methods (see Phosphoric Acid, Hydrochloric Acid).

Toxicity

The compound is strongly irritating to skin, eyes and mucous membranes.

PHOSPHORUS PENTAFLUORIDE

[7647-19-0]

Formula: PF_5 ; MW 125.97

Synonym: phosphorus(V)fluoride

Uses

Phosphorus pentafluoride is a catalyst in ionic polymerization reactions.

Physical Properties

Colorless gas; fumes in air; density 5.527g/L; heavier than air, density in air 4.35 (air=1); liquefies at -84.6°C ; freezes at -93.8°C ; reacts with water.

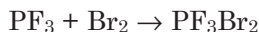
Thermochemical Properties

ΔH_f°	-381.1 kcal/mol
ΔG_f°	-363.5 kcal/mol
S°	1.9 cal/deg mol
C_p	20.3 cal/deg mol
ΔH_{ap}	4.11 kcal/mol

Preparation

Phosphorus pentafluoride may be prepared by several methods, among which are:

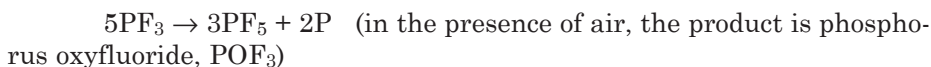
1. Treating phosphorus trifluoride with bromine and then heating the product phosphorus trifluoride dibromide, PF_3Br_2 :



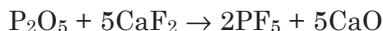
2. Heating phosphorus pentachloride with arsenic trifluoride:



3. Subjecting phosphorus trifluoride to an electric spark in the absence of air (a disproportionation reaction occurs):



4. Heating a mixture of phosphorus pentoxide and calcium fluoride:



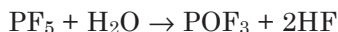
5. Heating a mixture of phosphorus oxyfluoride, hydrogen fluoride and sulfur trioxide:



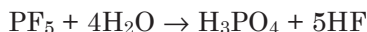
The gas should be stored in steel cylinders in the absence of moisture.

Reactions

Phosphorus pentafluoride hydrolyzes in water, the products formed depend on the reaction conditions. When exposed to moisture it forms phosphorus oxyfluoride:



Hydrolysis with water proceeds through formation of intermediates, oxyfluorophosphates and ultimately gives phosphoric acids. The overall reaction may be written as follows:



The pentafluoride also is known to form adducts. With nitrogen dioxide it forms an adduct, $\text{PF}_5 \cdot \text{NO}_2$, at -10°C which decomposes on warming.

Many complexes also are known, particularly with amines, pyridine, sulfoxides, and ethers.

Analysis

Elemental composition: P 24.59%, F 75.41%. The compound may be completely hydrolyzed in water and the ultimate hydrolysis products, phosphoric acid and HF, may be determined for PO_4^{3-} and F^- by ion chromatography. The compound may be confirmed by GC/MS. Its diluent mixture in helium or other inert gas may be introduced onto the GC column and PF_5 may be identified from its mass spectra. The characteristic mass ions are 126, 31, 107.

Toxicity

Phosphorus pentafluoride is a highly toxic gas. Inhalation can cause severe irritation of mucous membrane and pulmonary edema. It is corrosive to skin and can damage eyes.

PHOSPHORUS PENTOXIDE

[1314-56-3]

Formula: P_2O_5 ; MW 141.95; exists as P_4O_{10} units as molecular entities

Synonyms: phosphorus pentaoxide; phosphorus(V) oxide; phosphoric anhydride

Uses

Phosphorus pentoxide is a very effective drying and dehydrating agent. It also converts acids to their anhydrides.

Physical Properties

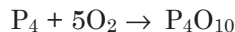
White, deliquescent, powdery solid; exhibits polymorphism; converts to several different crystalline forms on heating; the commercial material consists of hexagonal crystals; the hexagonal crystals on very rapid heating first melt at 420°C and then resolidify immediately to glassy orthorhombic crystals; slow heating of hexagonal crystals causes melting at 340°C which, on solidification, gives the same metastable orthorhombic form; the glassy material melts at about 580°C to a colorless and heavily viscous liquid; sublimates at 360°C ; density of the commercial product 2.39 g/cm^3 ; reacts with water.

Thermochemical Properties

ΔH_f° (hexagonal)	-713.2 kcal/mol
ΔH_f° (amorphous)	-727.0 kcal/mol
ΔG_f° (hexagonal)	-644.8 kcal/mol
S° (hexagonal)	54.7 cal/deg mol
C_p (hexagonal)	50.6 cal/deg mol

Preparation

Phosphorus pentoxide is prepared by burning phosphorus in a plentiful supply of dry air or oxygen:



The crude product may contain a small amount of sesquioxide, P_2O_3 , which may be removed by sublimation in ozonized oxygen.

Reactions

The most important reaction of phosphorus pentoxide is its hydrolysis. The hexagonal form reacts with water vigorously to form metaphosphoric acid $(\text{HPO}_3)_n$ which hydrolyzes further to yield phosphoric acid, H_3PO_4 :



In finely divided hexagonal form, the compound reacts violently with water. The orthorhombic allotrope reacts much less vigorously than the hexagonal form.

Phosphorus pentoxide dehydrates nitric acid at low temperatures (about -10°C) forming metaphosphoric acid and nitrogen pentoxide:



Reaction with phosphorus pentabromide yields phosphorus oxybromide:

**Analysis**

Elemental composition: P 43.64%, O 56.36%. The pentoxide is dissolved in water and the ultimate hydrolysis product, H_3PO_4 , is analyzed for PO_4^{3-} by ion chromatography. Alternatively, the solution is treated with ammonium molybdate—ammonium vanadate reagent to produce a yellow colored vanadomolybdophosphoric acid. Absorbance or transmittance of the solution may be measured at a wavelength between 400 to 490 nm, depending on concentration of PO_4^{3-} . The solution must be diluted for analysis. The solution may further be reduced with stannous chloride to form an intensely colored molybdenum blue for measuring absorbance or transmittance at 690nm.

Toxicity

Phosphorus pentoxide is a strong irritant. It is corrosive to skin and contact with eyes can be injurious.

PHOSPHORUS TRICHLORIDE

[7719-12-2]

Formula: PCl_3 ; MW 137.33

Uses

Phosphorus trichloride is used to prepare phosphine and other phosphorus compounds.

Physical Properties

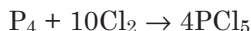
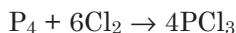
Colorless fuming liquid; pungent odor; refractive index 1.516 at 14°C; density 1.574g/mL at 21°C; boils at 76°C; freezes at -112°C; decomposes in water; soluble in benzene, carbon disulfide, ether and chloroform and other halogenated organic solvents.

Thermochemical Properties

ΔH_f° (liq)	-76.4 kcal/mol
ΔH_f° (gas)	-68.6 kcal/mol
ΔG_f° (liq)	-65.1 kcal/mol
ΔG_f° (gas)	-64.0 kcal/mol
S° (liq)	74.5 cal/deg mol
C_p (liq)	17.17 cal/deg mol

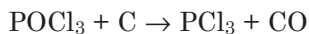
Preparation

Phosphorus trichloride is prepared by reacting white phosphorus with dry chlorine present in limited quantity. Excess chlorine will yield phosphorus pentachloride, PCl_5 .



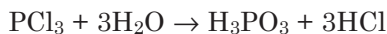
The compound is prepared in a retort attached to inlet tubes for dry chlorine and dry carbon dioxide and a distillation flask. White phosphorus is placed on sand in the retort. All air, moisture, and any phosphorus oxide vapors present in the apparatus are expelled by passing dry carbon dioxide. Dry chlorine is then introduced into the apparatus. If a flame appears on phosphorus it indicates presence of excess chlorine. In that event, the rate of chlorine introduction should be decreased. For obtaining phosphorus trichloride, flame should appear at the end of the chlorine-entry tube. The trichloride formed is collected by condensation in the distillation flask. A soda lime tube is attached to the apparatus to prevent moisture entering the flask.

Phosphorus trichloride also can be prepared by reducing phosphorus oxychloride vapors with carbon at red heat:



Reactions

Phosphorus trichloride reacts violently with water forming phosphorus acid:



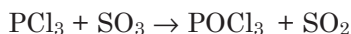
When dry chlorine gas is passed into the liquid trichloride under cooling, phosphorus pentachloride is obtained:



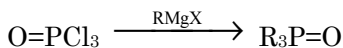
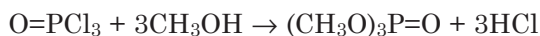
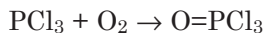
Phosphorus trichloride reacts with concentrated sulfuric acid forming chlorosulfuric acid and metaphosphoric acid:



Reaction with sulfur trioxide produces phosphoryl chloride:



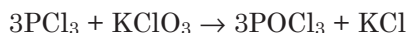
Oxidation of trichloride produces phosphorus trichloride oxide which may be used as the starting material to prepare alkyl- and alkoxyphosphine oxides:



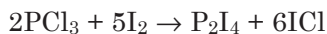
Phosphorus trichloride reacts with thionyl chloride to form phosphoryl chloride, thiophosphoryl chloride and phosphorus pentachloride:



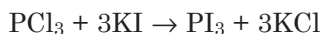
It reacts violently with potassium chlorate forming phosphoryl chloride:



Phosphorus trichloride reacts with iodine in warm glacial acetic acid solution, which on cooling yields orange crystals of phosphorus diiodide:

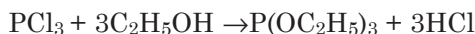


Reaction with potassium iodide yields phosphorus triiodide:

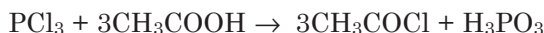


Phosphorus trichloride reacts with organics that contain hydroxyl groups.

However, with ethanol two competing reactions occur:



With acetic acid the products are acetyl chloride and phosphorus acid:

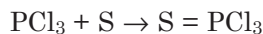


Similar reactions occur with other carboxylic acids.

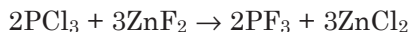
Reactions with ammonia under controlled conditions produce phosphorus triamine:



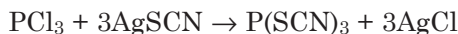
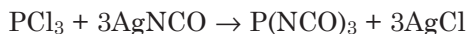
Reaction with sulfur forms phosphorus trichloride sulfide:



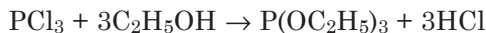
Phosphorus trichloride is converted to phosphorus trifluoride by heating with fluoride of arsenic, antimony or zinc:



Reaction with silver isocyanate or silver thiocyanate yields phosphorus triisocyanate or phosphorus trithiocyanate:

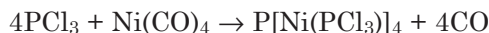


Reaction with lower alcohols in the presence of a base yields the corresponding trialkoxyphosphine:



However, in the absence of a base the product is dialkoxyphosphine oxide, $(\text{C}_2\text{H}_5\text{O})_2\text{PH}(=\text{O})$.

Phosphorus trichloride forms a tetracoordinated nickel complex by action with nickel tetracarbonyl:



Analysis

Phosphorus trichloride may be dissolved in a suitable organic solvent such as benzene or chloroform and analyzed by GC-NPD in phosphorus mode. Its

solution in CS₂ may be analyzed by GC—FID. The most definitive test is by mass spectrometry.

Hazard

Phosphorus trichloride is highly corrosive. Its vapors are an irritant to mucous membranes. Chronic exposure to its vapors can cause bronchitis. It reacts violently with water and explodes in contact with acetic and nitric acids, and several other substances (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd. Ed. New York: John Wiley & Sons).

PLATINIC ACID, HEXACHLORO

[16941-12-1]

Formula: H₂PtCl₆; MW 409.81; crystallized as a hexahydrate, H₂PtCl₆ • 6H₂O
Synonyms: chloroplatinic acid; hexachloroplatinic acid; hexachloro platinum-(IV) acid

Uses

Chloroplatinic acid is used in preparing most platinum salts and complexes. It also is used as an electroplating bath for plating and coating of platinum. Other applications are in catalysis.

Physical Properties

The hexahydrate consists of red to brownish-red cubic crystals; deliquesces; density 2.431g/cm³; melts at 60°C; very soluble in water and alcohol; soluble in ether.

Preparation

Hexachloroplatinic acid is obtained in an intermediate step during extraction of platinum from minerals. The compound is formed when platinum is dissolved in aqua regia containing a higher proportion of HCl and subsequently is evaporated repeatedly with hydrochloric acid, preferably in a chlorine atmosphere. Alternatively, hexachloroplatinic acid may be obtained by dissolving platinum tetrachloride, PtCl₄, in water.

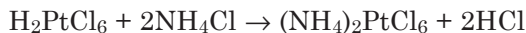
Pure hexachloroplatinic acid may be prepared by dissolving platinum sponge in hydrochloric acid under chlorine.

Reactions

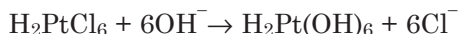
Hexachloroplatinic acid decomposes completely when ignited, leaving a residue of spongy platinum. Hexachloroplatinic acid on heating at 300°C in chlorine forms platinum tetrachloride:



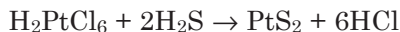
Reactions with ammonium chloride or other ammonium salts form a lemon yellow precipitate of ammonium hexachloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$:



Treatment with caustic alkali yields a white precipitate of hexahydroxoplatinic acid, $\text{H}_2\text{Pt}(\text{OH})_6$:

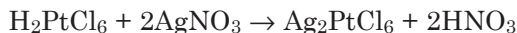


When hydrogen sulfide is bubbled into a boiling solution of hexachloroplatinic acid, a black precipitate of platinum disulfide, PtS_2 (soluble in aqua regia) is obtained:



The above reaction is accompanied simultaneously with reduction of $[\text{PtCl}_6]^{2-}$ into platinum in metallic state. Metallic platinum, however, is a minor product.

Addition of silver nitrate produces a yellow precipitate of silver hexachloroplatinate, Ag_2PtCl_6 :



Hexachloroplatinic acid may be reduced to tetrachloroplatinic(II) acid, H_2PtCl_4 , by sulfur dioxide and other reducing agents.

Analysis

Elemental composition (anhydrous salt): Pt 47.60%, H 0.49%, Cl 51.90%. The compound may be identified by its physical and chemical properties. Platinum in an aqueous solution of the compound can be analyzed by flame AA or ICP spectroscopy. Also, the compound can be measured by gravimetry following precipitation with ammonium chloride, hydrogen sulfide, or silver nitrate (see Reactions above).

PLATINUM

[7440-06-4]

Symbol Pt; atomic number 78; atomic weight 195.08; a Group VIII (Group 10) noble metal; atomic radius 1.39Å; ionic radius of Pt^{2+} and Pt^{4+} in crystals having coordination numbers 4 and 6 are 0.60 Å and 0.63Å respectively; electron configuration $[\text{Xe}]4f^{14}5d^96s^1$; valence states +2, +3, +4, most common valence +4; six stable isotopes: Pt-190 (0.011%), Pt-192 (0.80%), Pt-194 (32.96%), Pt-195 (33.86%), Pt-196 (25.36%), Pt-198 (7.22%); twenty-nine radioactive isotopes in the mass range 168–190, 193, 197, 199–202; the longest lived radioactive isotope is naturally occurring Pt-190, $t_{1/2}$ 6.5×10^{11} years.

History, Occurrence, and Uses

Platinum was discovered in Colombia, South America by Ulloa in 1735 and six years later in 1741 by Wood. The metal was isolated from native platinum by de l'Isle in 1775 and produced in malleable form by Chabaneau in 1786. Wollaston in 1803 developed a method of obtaining pure malleable platinum from crude platinum by extraction with aqua regia. The process led to the discovery of two other platinum group metals, palladium and rhodium, that were found in the aqua regia extract after platinum precipitated. Platinum derived its name from *platina* originating from the Spanish word *plata* for silver, because it was thought to be a trivial unwanted material associated with gold in gold mines of Central America.

Platinum occurs in nature as a bright-white cubic crystalline solid with metallic luster associated with other noble metals of its group. Platinum also occurs as the mineral sperrylite, PtAs_2 , found as tin-white brittle cubic crystals containing 52–57% platinum in certain nickel-bearing deposits. Some other minerals of platinum are cooperite PtS (Pt 80-86%); and braggite (Pt, Pd, NiS (Pt 58-60%). The abundance of platinum in the earth's crust is estimated to be 0.005 mg/kg.

Platinum metal and its alloys have numerous applications. As a precious metal it is used extensively in jewelry. Other important applications include construction of laboratory crucibles and high temperature electric furnaces; in instruments as thermocouple elements; as wire; for electrical contacts; as electrodes; in dentistry; in cigarette lighters; and for coating missile and jet engine parts.

Platinum also is used extensively as a catalyst in hydrogenation, dehydrogenation, oxidation, isomerization, carbonylation, and hydrocracking. Also, it is used in organic synthesis and petroleum refining. Like palladium, platinum also exhibits remarkable ability to absorb hydrogen. An important application of platinum is in the catalytic oxidation of ammonia in Ostwald's process in the manufacture of nitric acid. Platinum is installed in the catalytic converters in automobile engines for pollution control.

Physical Properties

Silvery-white lustrous metal; remains bright at all temperatures; face-centered cubic crystal; density 21.5g/cm^3 ; Vickers hardness, annealed 38-40; melts at $1,768.4^\circ\text{C}$; vaporizes at $3,825^\circ\text{C}$; vapor pressure at melting point 0.00014 torr; electrical resistivity 9.85 microhm-cm at 0°C ; magnetic susceptibility $9.0 \times 10^{-6}\text{ cm}^3/\text{g}$; Poisson's ratio 0.39; thermal neutron cross section 8 barns; insoluble in water and acids; soluble in aqua regia

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	135.1 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	124.4 kcal/mol
S° (cry)	9.94 cal/deg mol
S° (gas)	46.0 cal/deg mol

C_p (cry)	6.19 cal/deg mol
C_p (gas)	6.09 cal/deg mol
ΔH_{fus}	5.30 kcal/mol
Thermal conductivity	71.1 W/(m.K)
Coefficient of linear expansion, at 20°C	$9.1 \times 10^{-6}/^\circ\text{C}$

Reactions

At ordinary temperatures platinum is inert to practically all substances except aqua regia and, to a small extent, chlorine water. The metal is not attacked by strong acids except aqua regia. It dissolves in aqua regia forming chloroplatinic acid, H_2PtCl_6 .

Platinum reacts with oxygen only at elevated temperatures. Finely divided metal forms platinum oxide, PtO , at about 500°C. When heated at 1,000°C in air or oxygen, platinum loses weight probably due to the evaporation of the thin layer of PtO_2 from its surface.

Fused alkalis, particularly potassium and barium hydroxides, are corrosive to platinum. In the presence of oxygen or oxidizing agents this corrosive action of fused alkalis increases. Also, cyanide and nitrates of alkali metals in fused state are corrosive to platinum.

Platinum combines with dry chlorine above 250°C forming platinum dichloride, PtCl_2 . Reaction with fluorine occurs at dull red heat forming platinum tetrafluoride, PtF_4 , as the major product, with small amounts of difluoride, PtF_2 .

Platinum can be alloyed with many elements at elevated temperatures. Such elements include other noble metals, as well as, cobalt, selenium, silicon, and arsenic and nonmetals like carbon, phosphorus, and sulfur.

Platinum, like palladium, absorbs a large volume of hydrogen, particularly when heated. Hydrogen also diffuses through hot platinum sheet.

Platinum retains hydrogen at ordinary temperature and gives off the gas when heated in vacuum.

Production

Platinum metal concentrate obtained after the mineral is subjected to various mechanical processes including froth flotation and gravity separation is treated with aqua regia. Gold, platinum and palladium dissolve in aqua regia leaving behind other noble metals and silver in the insoluble residues. Gold is precipitated from the aqua regia extract by treating the solution with dibutyl carbitol. Alternatively, gold may be removed from the chloride solution by reduction with sulfur dioxide or ferrous salt to yield metallic gold. The filtrate solution contains platinum and palladium in the form of chloroplatinic and chloropalladic acids, H_2PtCl_6 and H_2PdCl_4 , respectively. Ammonium chloride is added to this solution to precipitate ammonium chloroplatinate $(\text{NH}_4)_2\text{PtCl}_6$ leaving palladium in solution. The precipitate obtained at this stage contains trace impurities. Crude complex is refined in a series of steps to obtain purified metal. Such refining steps may include igniting the complex; dissolving the impure platinum sponge in aqua regia; treatment with sodium chloride to precipitate sodium platinum chloride, Na_2PtCl_6 , and converting pure

Na_2PtCl_6 to ammonium platinum chloride $(\text{NH}_4)_2\text{PtCl}_6$. The purified ammonium complex is then ignited to form platinum sponge.

Analysis

Platinum in metallic form is brought into aqueous phase by boiling with aqua regia and evaporating almost to dryness. This is followed by adding concentrated HCl and a small amount of NaCl and again evaporating to dryness. Finally, the residue is dissolved in dilute HCl and diluted further for analysis. The aqueous solution is analyzed by flame-atomic absorption spectrophotometry using an air-acetylene flame. Measurement may be carried out at the wavelength 265.9 nm. Platinum may be measured by other instrumental techniques such as X-ray fluorescence and neutron activation analysis.

PLATINUM DICHLORIDE

[10025-65-7]

Formula: PtCl_2 ; MW 265.99

Synonyms: platinum(II) chloride; platinous chloride

Uses

The compound does not have any notable commercial applications. It is used to prepare tetrachloroplatinic(II) acid (chloroplatinous acid) and tetrachloroplatinate salts.

Physical Properties

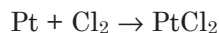
Olive green hexagonal crystals; density 6.05 g/cm^3 ; decomposes to platinum metal and chlorine on heating at 581°C ; insoluble in water and alcohol; soluble in hydrochloric acid and ammonia solution.

Thermochemical Properties

$$\Delta H_f^\circ \quad -29.5 \text{ kcal/mol}$$

Preparation

Platinum dichloride is prepared by heating platinum sponge in chlorine at about 500°C :



It also may be obtained by thermal decomposition of platinum tetrachloride, PtCl_4 , or hexachloroplatinic acid:



Reactions

Platinum dichloride dissolves in hydrochloric acid to form a dark brown complex acid, tetrachloroplatinic(II) acid, H_2PtCl_4 in the solution:



Tetrachloroplatinic(II) acid formed above may decompose to a small extent forming metallic platinum and hexachloroplatinic(II) acid.

Reactions with carbon monoxide at moderate temperatures yield complexes $[\text{PtCl}_2(\text{CO})_2]$, $[\text{PtCl}_2(\text{CO})_2]$, and $[(\text{PtCl}_2)_2(\text{CO})_2]$, having melting points 194°, 142°, and 130°C, respectively.

Platinum dichloride forms complexes with ammonia, $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, which on heating yields $[\text{PtCl}_2(\text{NH}_3)_2]$.

Analysis

Elemental composition: Pt 73.36%, Cl 26.64%. The compound is dissolved in concentrated HCl, diluted, and analyzed for platinum by flame-AA spectrophotometry (see Platinum). The salt may be identified by its olive green color and other physical and x-ray properties. It forms a dark brown color in HCl.

PLATINUM DIOXIDE

[1314-15-4]

Formula: PtO_2 ; MW 227.08; forms mono-, di-, and tetrahydrates

Synonyms: platinum(IV) oxide; platonic oxide; Adams' catalyst

Uses

Platinum dioxide, also known as Adams' catalyst, is used commercially in many hydrogenation reactions at ordinary temperatures, such as reduction of olefinic and acetylenic unsaturation, aromatics, nitro, and carbonyl groups.

Physical Properties

Black solid; density 10.2 g/cm³; melts at 450°C; thermally decomposes; insoluble in water, alcohol, acids and aqua regia; soluble in caustic potash solution.

Thermochemical Properties

ΔH_f° (g)	41.0 kcal/mol
ΔG_f° (g)	40.1 kcal/mol

Preparation

Platinum dioxide is obtained as its monohydrate, $\text{PtO}_2 \cdot \text{H}_2\text{O}$, a brown-red precipitate, upon boiling a solution of platinum tetrachloride, PtCl_4 , with sodium carbonate.

The anhydrous black dioxide, PtO_2 , may be prepared by treating a solution

of hexachloroplatinic acid, H_2PtCl_6 , with sodium carbonate. The yellow hexahydroxoplatinic acid, $\text{H}_2\text{Pt}(\text{OH})_6$, is carefully heated below 100°C to yield the black PtO_2 . Strong heating may decompose the dioxide to platinum metal.

Analysis

Elemental composition: Pt 85.91%, O 14.09%. The oxide may be characterized by its physical properties and by x-ray diffraction. The compound may be thermally decomposed at elevated temperatures or reduced by hydrogen to form platinum metal which may be digested with aqua regia and HCl, diluted, and analyzed by flame AA, ICP/AES or ICP/MS.

PLATINUM HEXAFLUORIDE

[13693-05-5]

Formula PtF_6 ; MW 309.07; monomeric in vapor phase; Pt–F bond length is about $1.82\text{\AA}$

Uses

Platinum hexafluoride does not have many commercial applications. It is used as a strong oxidizing agent and can oxidize oxygen from the air. It is used in research. Platinum hexafluoride forms compounds with molecular oxygen and xenon, $[\text{O}_2^+][\text{PtF}_6^-]$ and XePtF_6 , respectively.

Physical Properties

Dark-red octahedral crystals; volatile and unstable; density 3.83g/cm^3 ; melts at 61.3°C ; vaporizes at 69.14°C ; reacts violently with water.

Preparation

Platinum hexafluoride may be prepared by heating platinum with fluorine under pressure. The preparation should be in nickel or Monel apparatus as the compound reacts with glass.

Reaction

The hexafluoride is a very powerful oxidizing agent reacting violently with most oxidizable substances. Reaction with liquid water is violent forming HF, oxygen, lower fluorides of platinum, and other products. In vapor phase hydrolysis occurs more smoothly.

The hexafluoride decomposes on heating; also decomposed by UV radiation to lower fluorides; and reacts with the inert gas xenon, forming a solid product, $\text{Xe}(\text{PtF}_6)$. It reacts with molecular oxygen to produce $\text{O}_2^+\text{PtF}_6^-$. The compound attacks glass at ordinary temperatures.

Hazard

Platinum hexafluoride is dangerously corrosive. Inhalation of its vapors or skin contact causes serious injury. Also, it can react explosively with a number of substances.

PLATINUM MONOXIDE

[12035-82-4]

Formula PtO; MW 211.08

Synonyms: platinum oxide; platinum(II) oxide

Uses

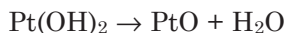
Platinum monoxide is used to prepare platinum-based catalysts.

Physical Properties

Violet-black solid; density 14.9g/cm³; decomposes on heating at 550°C; insoluble in water and alcohol; soluble in aqua regia.

Preparation

Platinum monoxide is prepared by thermal decomposition of platinum(II) hydroxide, Pt(OH)₂, under careful heating.



If the hydroxide is heated too strongly and rapidly it disproportionates forming platinum metal and platinum dioxide:



Platinum monoxide may be obtained as a black precipitate when an alkali hydroxide is added to an aqueous solution of potassium tetrachloroplatinate(II) (potassium chloroplatinate), K₂PtCl₄.

Analysis

Elemental composition: Pt 92.41%, O 7.59%. The oxide can be identified by its physical and x-ray properties. Additionally, platinum may be measured by flame-AA following digestion of the solid with aqua regia and HCl (see Platinum).

PLATINUM TETRACHLORIDE

[37773-49-2]

Formula: PtCl₄; MW 336.89; also forms a pentahydrate, PtCl₄ • 5H₂O

Synonyms: platinum(IV) chloride; platonic chloride

Uses

Platinum tetrachloride is used to prepare chloroplatinic acid and many platinum complexes, particularly with ammonia. Such complexes were pre-

pared and studied by Alfred Werner to support his theory on coordination compounds.

Physical Properties

Brown-red crystalline solid; density 4.303g/cm³; decomposes at 370°C; readily dissolves in water; dissolves in hydrochloric acid forming chloroplatinic acid, H₂PtCl₆; soluble in acetone; slightly soluble in ethanol; insoluble in ether.

The pentahydrate PtCl₄•5H₂O constitutes red monoclinic crystals; density 2.43g/cm³; loses water on heating; very soluble in water; soluble in alcohol and ether.

Thermochemical Properties

$$\Delta H_f^\circ \text{ (g)} \quad -55.4 \text{ kcal/mol}$$

Preparation

Platinum tetrachloride is prepared by decomposition of hexachloroplatinic(IV) acid, H₂PtCl₆, in a stream of chlorine gas at 300°C.

Analysis

Elemental composition: Pt 52.56%, Cl 47.44%. Platinum tetrachloride may be dissolved in water and analyzed for platinum (see Platinum). Also, it may be identified by its physical properties and certain precipitation reactions after dissolving in HCl (see Platinic Acid, Hexachloro).

PLUTONIUM

[7440-07-5]

Symbol Pu; atomic number 94; atomic weight 244; an actinide series transuranium element; a man-made radioactive element; electron configuration [Rn]5f⁶7s²; partially filled *f* subshell; valence states +3, +4, +5, +6; eighteen isotopes in the mass range 228-230, 232-246; all isotopes radioactive; the longest lived isotope Pu-244, *t*_{1/2} 8.2x10⁷ year; the shortest lived isotope Pu-233, *t*_{1/2} 20.9 minute.

History, Occurrence, and Uses

Plutonium was discovered by Wahl, Seaborg, and Kennedy in 1941 at Berkeley, California when they separated and identified its isotope of mass 238 produced from bombarding uranium isotopes with neutrons in a cyclotron. In the same year the isotope Pu-239 was found to be fissionable. However, only microgram quantities of Pu-239 were generated by cyclotron bombardment. In 1943 Enrico Fermi and his group developed a process for successful generation of much larger quantities of plutonium for nuclear weapons. They achieved a self-sustaining nuclear chain reaction in a reactor

using uranium and graphite. This work eventually led to the first successful testing of an atom bomb in the desert of New Mexico in July 1945.

Plutonium is the second transuranium element after neptunium. The element was named after the planet Pluto.

Plutonium is the most important transuranium element. Its two isotopes Pu-238 and Pu-239 have the widest applications among all plutonium isotopes. Plutonium-239 is the fuel for nuclear weapons. The detonation power of 1 kg of plutonium-239 is about 20,000 tons of chemical explosive. The critical mass for its fission is only a few pounds for a solid block depending on the shape of the mass and its proximity to neutron absorbing or reflecting substances. This critical mass is much lower for plutonium in aqueous solution. Also, it is used in nuclear power reactors to generate electricity. The energy output of 1 kg of plutonium is about 22 million kilowatt hours. Plutonium-238 has been used to generate power to run seismic and other lunar surface equipment. It also is used in radionuclide batteries for pacemakers and in various thermoelectric devices.

Physical Properties

Silvery-white metal; warm to touch because of its ionizing radiation; when in appreciable amounts the metal can generate enough heat to boil water; attains yellowish appearance when slightly oxidized. Six allotropic modifications are known: (1) alpha monoclinic form with sixteen atoms per unit cell; stable at ordinary temperatures; density 19.86g/cm³; converts to beta form at 115°C. (2) beta form; body-centered monoclinic crystal structure; thirty-four atoms per unit cell; density 17.70 g/cm³; stable between 115 to 200°C; converts to gamma form at about 200°C. (3) gamma modification; face-centered orthorhombic structure; eight atoms in unit cell; density 17.14g/cm³; exists between 200 to 310°C; converts to delta form at 310°C. (4) delta allotrope; face-centered cubic structure; four atoms per unit cell; density 15.92g/cm³; stable in the temperature range 310 to 452°C; converts to a delta-prime form at 452°C. (5) delta-prime form; body-centered tetragonal crystals; two atoms per unit cell; density 16.00g/cm³; stable between 452 to 480°; converts to another allotropic form, known as epsilon at 480°C. (6) epsilon form; body-centered cubic structure; two atoms per unit cell; density 16.51g/cm³; stable at temperatures between 480 to 640°C.

Plutonium melts at 640°C; vaporizes at 3,228°C; electrical resistivity 146.4 microhm-cm at 0°C; Young's modulus 14x10⁶ psi; Poisson's ratio 0.17; dissolves in concentrated hydrochloric, hydriodic, and perchloric acids (with reaction).

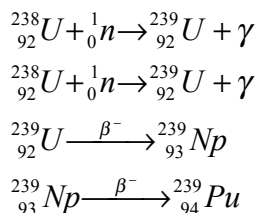
Thermochemical Properties

ΔH_f°	0.0
Thermal conductivity	0.0674 W/cmK
Coefficient of linear expansion	46.7 x 10 ⁻⁶ /°C
C_p	8.84 cal/g-atom
C_p (liquid at 675°C)	10.0 cal/g-atom
$\Delta H_{\alpha \rightarrow \beta}$	900 ± 20 cal/g-atom

$\Delta H\beta \rightarrow \gamma$	$160 \pm 10 \text{ cal/g-atom}$
$\Delta H\gamma \rightarrow \delta$	$148 \pm 15 \text{ cal/g-atom}$
$\Delta H\delta \rightarrow \delta'$	$10 \pm 10 \text{ cal/g-atom}$
$\Delta H\delta' \rightarrow \epsilon$	$444 \pm 10 \text{ cal/g-atom}$
$\Delta H\epsilon \rightarrow \text{liquid}$	$676 \pm 10 \text{ cal/g-atom}$

Production

Plutonium is produced from natural uranium which is a mixture of nonfissionable uranium-238 (99.3%) and fissionable uranium-235 (0.7%). The first synthesis of this element was in a cyclotron generating plutonium in microgram quantities. The isotope Pu-239 can be produced in much larger quantities in a nuclear reactor, either a conventional thermal reactor or a breeder type reactor by neutron bombardment of uranium-238. The nuclear reactions are shown below.



Higher isotopes such as Pu-240, -241, -242, etc. can be obtained from Pu-239 by continued neutron bombardment.

Plutonium-239 also is produced from natural uranium by the so-called "pile reactions" in which irradiation of uranium-235 isotope with neutrons produces fission, generating more neutrons and high energy (~200 MeV). These neutrons are captured by the uranium-238 to yield plutonium-239.

Synthesis of plutonium in significant quantities requires a sufficiently long reactor fuel irradiation period. Uranium, plutonium, and the fission products obtained after neutron irradiation are removed from the reactor and stored under water for several weeks. During such cooling periods most neptunium-239 initially formed from uranium and present in the mixture transforms to plutonium-239. Also, the highly radioactive fission products, such as xenon-133 and iodine-131 continue to decay during this period.

Plutonium is recovered from uranium and fission products by solvent extraction, precipitation, and other chemical methods. In most chemical processes, plutonium first is converted to one of its salts, usually plutonium fluoride, before it is recovered in purified metallic form. The fluoride is reduced with calcium metal to yield plutonium. Electrorefining may produce material of higher purity.

Plutonium is cast into small ingots by arc melting. All melting operations must be carried out in vacuum or in an inert atmosphere to prevent any air oxidation at high temperatures. Also, being a reactive metal, its recovery and purification should be done in crucibles made of highly refractory and stable materials.

Reactions

Plutonium is a reactive metal forming mostly tri-, tetra-, and hexavalent compounds. The solutions of Pu^{3+} are blue. The trivalent Pu^{3+} is stable in solution in the absence of air. In the presence of air or oxygen, Pu^{3+} slowly oxidizes to Pu^{4+} . In cold acid medium, permanganate ion oxidizes Pu^{3+} to Pu^{4+} . In aqueous solutions Pu^{4+} salts impart pink or greenish color to the solutions. Tetravalent Pu^{4+} converts to hexavalent plutonium, Pu^{6+} by the action of strong oxidizing agents, such as dichromate, $\text{Cr}_2\text{O}_7^{2-}$, permanganate, MnO_4^- or Ce^{4+} salts.

The metal ion in higher oxidation states can be reduced by most common reducing agents, such as, sulfur dioxide, carbon monoxide, ferrocyanide ion, hydrazine hydrochloride, and hydroxylamine hydrochloride to form Pu^{3+} (or Pu^{4+}) ions in solution.

Plutonium combines with oxygen at high temperatures to form plutonium dioxide, PuO_2 , and other oxides. The dioxide also is formed in the presence of water vapor. Ignition of the metal in air at $1,000^\circ\text{C}$ yields PuO_2 .

Plutonium reacts with hydrogen at high temperatures forming hydrides. With nitrogen, it forms nitrides, and with halogens, various plutonium halides form. Halide products also are obtained with halogen acids. Reactions with carbon monoxide yields plutonium carbides, while with carbon dioxide, the products are both carbides and oxides. Such reactions occur only at high temperatures.

Plutonium forms several complexes in oxidation states +3, +4, and +6.

Hazard

Plutonium is one of the most dangerous substances known. The metal and its salts are all highly toxic. Its ionizing radiation can cause cancer. The metal can incorporate with bone marrow forming insoluble plutonium (IV) phosphate. The metal only leaves the body very slowly. All operations must be carried out by remote control devices with proper shields. In production, processing, handling, and storage of large quantities of plutonium or its compounds one must bear in mind its critical mass, which can vary with the shape and the specific solid form or the quantities of plutonium contained in solutions.

POLONIUM

[7440-08-6]

Symbol Po; atomic number 84; atomic weight 209; a Group VIA (Group 16) radioactive element; electron configuration $[\text{Xe}]4f^{14}5d^{10}6s^26p^4$; valence states -2, 0, +2, +4, +6; atomic radius $1.64\text{\AA}$; atomic volume 23.53cc/g-atom ; the last radioactive member of radium series; twentyfive isotopes; all radioactive; the longest lived isotope is the alpha emitter Po-209, $t_{1/2} 105 \pm 5$ year.

History, Occurrence, and Uses

Polonium was discovered by Marie Curie in 1898 while investigating the radioactivity of pitchblende. Mme. Curie named this new element after her native country Poland. Polonium is a very rare element, found in exceedingly small quantities in uranium ores. Its abundance in uranium ore is about 100mg/ton. Its applications are only a few. Polonium is used on brushes to remove dusts from photographic film. It also is used in instruments to eliminate static charges. Polonium is used as a small source to generate alpha particles and neutrons; as a power source in devices where its radioactive decay energy is converted into electrical energy. For this application the metal is combined with lighter elements.

Physical Properties

Two crystalline forms exist; (1) alpha allotrope; a simple cubic low temperature form; density 9.196 g/cm³, and (2) beta modification: a rhombohedral high temperature form; density 9.398 g/cm³

Both allotropic forms coexist between 18 to 54°C; melt at 254°C; vaporize at 962°C; electrical resistivity 42 and 44 microhm-cm at 0°C for alpha- and beta- forms, respectively; practically insoluble in water; soluble in dilute mineral acids.

Thermochemical Properties

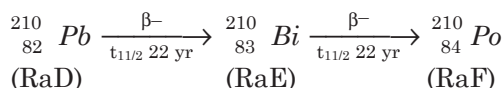
ΔH_f°	0.0
ΔG_f°	0.0
ΔH_{vap}	24.6 kcal/mol
ΔH_{sub}	34.5 kcal/g-atom
Coeff. linear expansion	$(23.0 \pm 1.5) \times 10^{-6}/^\circ\text{C}$

Production

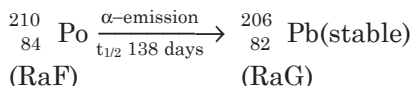
Polonium can be recovered from natural pitchblende. The yield, however, is exceedingly small as 1 g of polonium is contained in about 25,000 tons of pitchblende. The element may be isolated from the pitchblende extract by deposition on a bismuth plate immersed in chloride solution.

Polonium can be produced from other sources, too, that offer much higher yield than pitchblende. Two such processes are as follows:

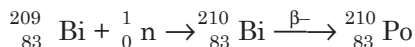
(1) The element may be obtained from radioactive lead-210 (also, known as RaD, the lead fraction in the extraction of radium from uranium ore) by successive beta decay:



The alpha emitter radioactive Po-210 that has a half-life of 138 days transforms to nonradioactive lead-206, the stable end product:



(2) Polonium also can be synthesized by neutron irradiation of natural bismuth in a reactor:



After neutron irradiation bismuth (canned in aluminum jackets) is dissolved in a mixture of hydrochloric and nitric acids and excess NO_3^- is removed by adding a reducing agent, such as, urea or formic acid. If bismuth is used as an anode, the reducing agent is dissolved in HCl. Various methods are applied for concentration of polonium in the acid mixture and its subsequent separation from bismuth. Such processes include spontaneous deposition of polonium over a less electropositive metal and coprecipitation with tellurium. In the latter method, a Te^{4+} or Te^{6+} salt is added to the extract, followed by addition of stannous chloride, which reduces both the tellurium and polonium to their metallic state, coprecipitating them from bismuth in the extract mixture.

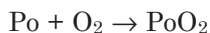
Another method to separate polonium from bismuth involves heating at 650°C to convert the metals into their oxides. This is followed by further heating to about 800°C at reduced pressure in which polonium metal is removed by volatilization.

Polonium may be purified by various processes. Such purification methods include precipitation of polonium as sulfide and then decomposing the sulfide at elevated temperatures; spontaneous decomposition of polonium onto a nickel or copper surface; and electrolysis of nitric acid solutions of polonium-bismuth mixture. In electrolytic purification polonium is electrodeposited onto a platinum, gold, nickel, or carbon electrode.

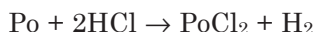
Reactions

Polonium resembles tellurium, the element above it in the same Group, in chemical behavior.

At ordinary temperatures polonium oxidizes slowly in air forming the basic oxide, PoO_2 :



The metal dissolves in dilute hydrochloric acid forming pink-red polonium dichloride:



The unstable dichloride converts to yellow tetrachloride, PoCl_4 .

Polonium dissolves in concentrated nitric acid and aqua regia, oxidizing to Po^{4+} state. Reaction with nitric acid forms adducts that probably have the compositions $4\text{PoO}_2 \cdot \text{N}_2\text{O}_5$; $4\text{PoO}_2 \cdot 3\text{N}_2\text{O}_5$ and $\text{Po}(\text{NO}_3)_4 \cdot \text{N}_2\text{O}_4$. The metal also dissolves in concentrated sulfuric and selenic acids forming polonium sulfate, $\text{Po}(\text{SO}_4)_2$ and $\text{Po}(\text{SeO}_4)_2$, respectively. Another product, $2\text{PoO}_2 \cdot \text{SO}_3$, also has been identified.

Because of its radioactivity and alpha emission, polonium forms many types of radiolytic oxidation-reduction products.

Analysis

At trace levels, polonium can be separated effectively by solvent extraction, ion exchange, paper chromatography, and other techniques. Diisopropyl ketone, di-n-octylamine, and tri-n-butylphosphate are suitable solvents for extraction. Trace amounts of polonium in solutions or solid mixtures containing no other emitters can be determined by measuring its alpha activity.

Hazard

As with other radioactive substances, exposure to its ionizing radiation can cause cancer. When ingested it tends to accumulate in the liver, kidney, and spleen causing radiation damage from the alpha particles. All operations and handling must be carried out in leak-proof boxes by mechanical means behind thick neutron shields.

POTASSIUM

[7440-09-7]

Symbol K; atomic number 19; atomic weight 39.098; a Group 1A (Group1) alkali metal element; atomic radius 2.35Å; ionic radius, K^+ 1.33Å; electron configuration $[\text{Ar}]4s^1$; valence state +1; ionization potential 4.341eV; standard redox potential, $E^\circ \text{K}^+ + e^- \leftrightarrow \text{K(s)} -2.925\text{V}$; three natural isotopes: K-39(93.258%), K-40 (0.0117%) and K-41 (6.730%); naturally occurring K-40 is radioactive, $t_{1/2}$ 1.25×10^9 year, beta emitter; fourteen synthetic radioisotopes in the mass range 35–38 and 42–51.

History, Occurrence, and Uses

Potassium was first isolated as a free metal in 1807 by Sir Humphry Davy. It was the first alkali metal to be discovered, produced by electrolysis of potassium carbonate (potash). The element was earlier called Kalium, derived from the Arabic word *qili*, meaning grass wort, the ash of which was a source of potash. The element derived its symbol K from Kalium. The English name potassium came from potash (pot ash), the carbonate salt of the metal.

Potassium is distributed widely in nature. The metal is too reactive to occur in native elemental form. It is the seventh most abundant element on earth, constituting 2.40% by weight of the earth's crust. It is abundantly present in sea water. Oceans contain 0.07% (wt to volume) potassium chloride.

Potassium occurs in many igneous rocks, such as, feldspar (potassium aluminum silicate), KAlSi_3O_8 (leucite) and mica, $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$. Disintegration of these rocks adds potassium to soil and water. Deposits of potassium chloride are found in practically all salt beds, associated with sodium chloride. Some important potassium minerals are leucite, KAlSi_2O_6 ; glauconite (a complex silicoaluminate structure of varying compositions); sylvite, KCl ; carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; langbeinite, $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$; and polyhalite, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Potassium, along with nitrogen and phosphorus, is an essential element needed for plant growth. In plants, it occurs mostly as K^+ ion in cell juice. It is found in fruit or seed. Deficiency can cause curling leaves, yellow or brown coloration of leaves, weak stalk and diminished root growth. Potassium deficiency has been associated with several common animal ailments. Potassium is in extracellular fluid in animals at lower concentrations than sodium.

Physical Properties

Silvery metal; body-centered cubic structure; imparts crimson-red color to flame; density 0.862g/cm^3 at 20°C ; melts at 63.25°C ; density of liquid potassium at 100°C is 0.819g/cm^3 and 0.771g/cm^3 at 300°C ; vaporizes at 760°C ; vapor pressure 123 torr at 587°C ; electrical resistivity 6.1 microhm-cm at 0°C and 15.31 microhm-cm at 100°C ; viscosity 0.25 centipoise at 250°C ; surface tension 86 dynes/cm at 100°C ; thermal neutron absorption cross section 2.07 barns; reacts violently with water and acids; reacts with alcohol; dissolves in liquid ammonia and mercury

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	21.33 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	14.49 kcal/mol
S° (cry)	15.34 cal/deg mol
S° (gas)	38.29 cal/deg mol
C_p (cry)	7.07 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	0.555 kcal/mol
ΔH_{vap}	0.496 kcal/mol
Thermal conductivity at 200°C	44.77 W/m.K

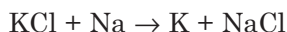
Production

Potassium can be produced by several methods that may be classified under three distinct types: (1) electrolysis, (2) chemical reduction, and (3) thermal decomposition.

Electrolysis processes have been known since Davy first isolated the metal in 1807. Electrolysis, however, suffers from certain disadvantages. A major problem involves miscibility of the metal with its fused salts. Because of this molten potassium chloride, unlike sodium chloride, cannot be used to produce the metal. Fused mixtures of potassium hydroxide and potassium carbonate

or chloride have been used as electrolytes with limited success.

Chemical reduction processes are employed nowadays in commercial, as well as, laboratory preparation of potassium. In one such process, molten potassium chloride is reduced with sodium at 760 to 880°C and the free metal is separated by fractionation:

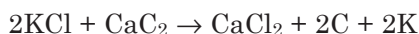
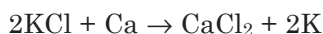
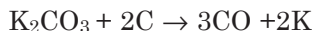


Potassium is obtained at over 99.5% purity. The metal, alternatively, may be alloyed with sodium for further applications.

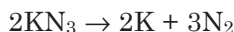
Reduction of potassium fluoride with calcium carbide at 1,000 to 1,100°C (Greisheim process) is an effective production method (Greer, J.S., Madaus, J.H and J.W. Mausteller. 1982. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. p. 914, New York: Wiley Interscience):



Some other chemical reduction methods that may be applied for laboratory generation of small quantities of potassium from its salts at high temperatures require a suitable reducing agent such as carbon, calcium, or calcium carbide:



Potassium can be produced by thermal decomposition of potassium azide:

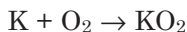
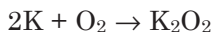
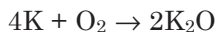


High purity metal may be produced by distillation of technical grade metal. Potassium (technical grade) may be packed under nitrogen. Argon should be used for packing high purity metal. Metal is shipped in stainless steel or carbon containers. In small quantities potassium is transported in glass or metal ampules.

Reactions

Potassium reacts with oxygen or air forming three oxides: potassium monoxide, K_2O ; potassium peroxide, K_2O_2 ; and potassium superoxide, KO_2 . The nature of the product depends on oxygen supply. In limited supply of oxygen potassium monoxide is formed, while in excess oxygen, superoxide is

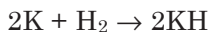
obtained:



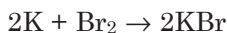
Potassium reacts violently with water, forming potassium hydroxide:



Potassium reacts with hydrogen at about 350°C to form potassium hydride:



Reactions with halogens, fluorine, chlorine and bromine occur with explosive violence. Thus, in contact with liquid bromine it explodes forming potassium bromide:

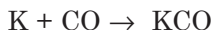


Potassium ignites in iodine vapor forming potassium iodide.

Violent reactions can occur with many metal halides. For example, with zinc halides or iron halides, single replacement reactions take place. Such potassium-metal halide mixtures can react violently when subjected to mechanical shock.

At ordinary temperatures, potassium does not combine with nitrogen but with an electric charge, potassium azide is formed.

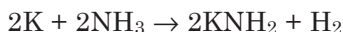
Reaction with carbon (graphite) at above 400°C produces a series of carbides, such as KC_4 , KC_8 , and KC_{24} . With carbon monoxide, an unstable explosive carbonyl forms:



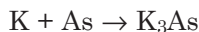
Potassium reduces carbon dioxide to carbon, carbon monoxide and potassium carbonate:



Potassium reacts with ammonia gas to form potassium amide with liberation of hydrogen:

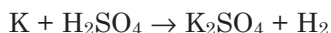


Reactions with phosphorus, arsenic and antimony form phosphide, arsenide, and antimonide of potassium, respectively:

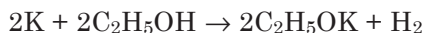


Reaction with sulfur forms three sulfides. When reactants are in molten state, the product is K_2S , but in liquid ammonia K_2S_2 and KS_2 are the main products.

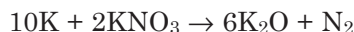
Potassium reacts explosively with sulfuric acid, forming potassium sulfate with evolution of hydrogen:



Potassium liberates hydrogen from ethanol forming potassium ethoxide:



Reaction with potassium nitrate yields potassium monoxide and nitrogen:



Analysis

Potassium and its salts can be identified by flame test. It imparts lilac color to the flame. Potassium ion in aqueous solution can be identified by reaction with sodium tetrphenylborate, $\text{NaB}(\text{C}_6\text{H}_5)_4$. In weakly acid solution, a white precipitate of the potassium salt $\text{KB}(\text{C}_6\text{H}_5)_4$ is obtained. The precipitate is filtered, dried, and weighed to measure potassium. The test is quantitative.

Potassium at trace concentrations in aqueous samples can be measured by a flame photometer at a wavelength of 766.5 nm. Either a flame photometer or an atomic absorption spectrometer operating in flame emission mode can be used for such analysis.

Potassium also can be measured by ICP/AES. The wavelengths at which it can be analyzed without interference from other metals are 766.49 and 769.90 nm. Other wavelengths may be used. Potassium ion in aqueous solution can be identified quantitatively by using a potassium ion-selective electrode attached to a pH meter having an expanded millivolt scale or to a specific ion meter having a direct readout concentration scale for potassium.

Hazard

Potassium metal can be dangerous to handle if proper precautions are not taken. Many of its reactions at ordinary temperatures can proceed to explosive violence (see Reactions). Also, it liberates flammable hydrogen gas when combined with water, acids, and alcohols.

POTASSIUM ACETATE

[127-08-2]

Formula: $\text{KC}_2\text{H}_3\text{O}_2$ or CH_3COOK ; MW 98.14

Uses

Potassium acetate is used in the manufacture of glass; as a softening agent for papers and textiles; as a dehydrating agent; and as a buffer. In medicine it is used as an expectorant and diuretic.

Physical Properties

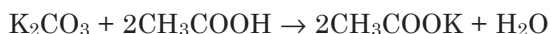
White lustrous powder or colorless deliquescent crystals; density 1.57 g/cm³; melts at 292°C; highly soluble in water, 253g/100mL at 20°C, more soluble in hot water, 492g/100mL at 62°C; aqueous solution alkaline, pH of 0.1M solution 9.7; soluble in methanol, ethanol and liquid ammonia; insoluble in ether and acetone.

Thermochemical Properties

ΔH_f° (cry)	-172.8 kcal/mol
ΔH_f° (amp)	-176.5 kcal/mol
ΔG_f° (amp)	-156.0 kcal/mol
S° (amp)	45.2 cal/deg mol
C_p (amp)	3.7 cal/deg mol

Preparation

Potassium acetate is prepared by addition of potassium carbonate in a small volume of water to acetic acid solution, followed by evaporation and crystallization:



Analysis

Elemental composition: K 39.85%, C 24.48%, H 3.08%, O 32.60%. Potassium may be identified by flame testing. An aqueous solution can be analyzed for potassium by flame photometry, ICP/AES, or ion selective electrode (see Potassium). Acetate anion may be measured in aqueous solution by ion chromatography under appropriate conditions.

POTASSIUM BICARBONATE

[298-14-6]

Formula KHCO₃; MW 100.12

Synonyms: potassium hydrogen carbonate; potassium acid carbonate

Uses

Potassium bicarbonate is used in baking powder and effervescent salts. In medicine, the salt is a gastric antacid and an electrolyte replenisher. It also is dry powder in fire extinguishers.

Physical Properties

Colorless transparent crystal or white powder; monoclinic structure; density 2.17 g/cm³; decomposes above 100°C; soluble in water, 22.49 g/100ml at 20°C, 60 g/100ml at 60°C pH of 0.1M aqueous solution 8.2; practically insoluble in alcohol.

Preparation

Potassium bicarbonate is obtained by passing carbon dioxide through a cold, concentrated solution of potassium carbonate:



Alternatively, KHCO₃ is produced by passing excess carbon dioxide through aqueous potassium hydroxide. At first, potassium carbonate is formed which then converts to the bicarbonate as shown in the above reaction.

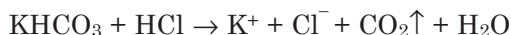
Potassium bicarbonate cannot be made by Solvay process because of its high solubility in water.

Reactions

Heating the bicarbonate yields normal carbonate, liberating carbon dioxide and water:



When the salt is added to dilute acids, carbon dioxide is liberated:



Reaction with caustic potash in solution forms potassium carbonate:

**Analysis**

Elemental composition: K 39.05%, C 11.99%, H 1.01%, O 47.94%. Potassium may be analyzed by AA spectroscopy in emission mode or by flame photometry (see Potassium). The aqueous solution may be treated with HCl and the CO₂ evolved may be noted from effervescence and tested by GC-TCD or by GC/MS. The characteristic mass ion for CO₂ is 44. Alternatively, the HCO₃⁻ anion or the CO₃²⁻ anion (converted by heating the bicarbonate) may be identified by ion chromatography.

POTASSIUM BISULFIDE

[1310–61–8]

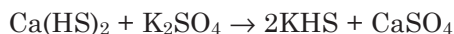
Formula KHS; MW 72.17; usually exists as a hemihydrate

Synonyms: potassium hydrosulfide; potassium hydrogen sulfide; potassium

sulfhydrate

Preparation

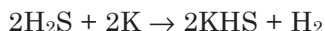
Potassium bisulfide is made by reacting calcium hydrogen sulfide with potassium sulfate:



The compound can be made by reacting hydrogen sulfide with potassium sulfide:



Purer compound may be produced by passing dry hydrogen sulfide through a solution of potassium metal dissolved in absolute ethanol:



Physical Properties

Colorless crystals or white crystalline mass; rapidly deliquesces; converts to a yellow rhombohedral crystalline mass upon exposure to air, forming polysulfides and H_2S ; density 1.68g/cm^3 ; the hemihydrate loses water at about 175°C ; melts at 455°C to a dark red liquid; decomposes in water; soluble in alcohol.

Thermochemical Properties

ΔH_f°	62.5 kcal/mol
ΔH_{soln} (at 17°C)	0.77 kcal/mol
ΔH_{soln} (hemihydrate at 16°C)	0.62 kcal/mol

Analysis

Elemental composition: K 54.18%, S 44.42%, H 1.40%. An aqueous solution may be analyzed for potassium by various methods (see Potassium). The compound on exposure to air evolves H_2S which can be detected from its odor, as well as by various tests (see Hydrogen Sulfide).

POTASSIUM BOROHYDRIDE

[13762-51-1]

Formula KBH_4 ; MW 53.95

Synonym: potassium tetrahydroborate

Uses

Potassium borohydride, unlike sodium borohydride, has very limited applications. The compound is a reducing agent.

Physical Properties

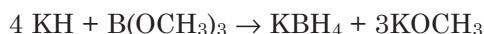
White crystalline solid; stable in air; nonhygroscopic; density 1.11g/cm³; decomposes at about 500°C without melting; soluble in water, 19g/100ml at 25°C; stable in alkaline solution; soluble in liquid ammonia and dimethyl formamide; slightly soluble in methanol, 0.7 g/100ml at 20°C.

Preparation

Potassium borohydride may be prepared by reacting potassium hydroxide with sodium borohydride. The salt precipitates from an aqueous solution of sodium borohydride with addition of potassium hydroxide:



Also, potassium borohydride can be made by reacting potassium hydride with methyl borate at high temperature:



Potassium borohydride also may be prepared by reacting potassium tetramethoxyborohydride with diborane at low temperatures; or by passing diborane through a solution of potassium methylate in methanol.

Analysis

Elemental composition: K 72.47%, B 20.06%, H 7.47%. The salt is dissolved in water and the solution analyzed for potassium and boron (see Potassium and Boron).

POTASSIUM BROMATE

[7758-01-2]

Formula: KBrO₃; MW 167.00

Uses

Potassium bromate is an oxidizing reagent in bromate-bromide mixture for titrimetric analysis. It also is a bread- and flour-improving agent.

Physical Properties

Colorless trigonal crystals or fine white crystals or granules; density 3.27 g/cm³ at 18°C; melts at 350°C; decomposes at about 370°C evolving oxygen; moderately soluble in water, 13.3 g/100mL at 40°C; slightly soluble in alcohol; insoluble in acetone.

Thermochemical Properties

ΔH_f°	-86.10 kcal/mol
ΔG_f°	-64.82 kcal/mol

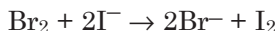
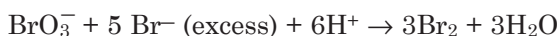
S°	35.65 cal/deg mol
C_p	28.72 cal/deg mol

Preparation

Potassium bromate can be produced by electrolysis of potassium bromide solution. Alternatively, the compound is obtained by adding potassium bromide to a saturated solution of sodium bromate or calcium bromate. The salt is recovered from solution by crystallization.

Analysis

Elemental composition: K 23.41%, Br 47.85%, O 28.74%. Aqueous solution of the salt after sufficient dilution may be analyzed for its potassium content by AA, ICP, or flame photometry (see Potassium) and for bromate anion by ion chromatography. Also, bromate content can be measured by iodometric titration using a standard solution of sodium thiosulfate and starch as indicator. The redox reactions are as follows:



Liberated iodine is titrated against a standard solution of thiosulfate until the starch solution's blue decolorizes.

Toxicity

Ingestion of the salt or its solution can cause nausea, vomiting, diarrhea, and renal injury. Also, it can induce methemoglobinemia.

POTASSIUM BROMIDE

[7758-02-3]

Formula: KBr; MW 119.00

Uses

Potassium bromide is used to make photographic plates and papers and in engraving. Other uses are as a brominating agent in organic synthesis and in the bromate-bromide mixture in titrimetric analysis. In medicine potassium bromide is a sedative and anticonvulsant.

Physical Properties

Colorless cubic crystals or white granules or powder; density 2.75 g/cm³ at 25°C; melts at 734°C; vaporizes at 1,435°C; readily dissolves in water, solubility at 0°C 53.5 g/100mL and at 100°C 102 g/100mL; aqueous solution neutral; soluble in glycerol, 21.7 g/100mL; sparingly soluble in boiling ethanol 4.76 g/100mL.

Thermochemical Properties

ΔH_f° (cry)	-94.12 kcal/mol
ΔH_f° (gas)	-43.04 kcal/mol
ΔG_f° (cry)	-90.98 kcal/mol
ΔG_f° (gas)	-50.89 kcal/mol
S° (cry)	22.92 cal/deg mol
S° (gas)	59.95 cal/deg mol
C_p (cry)	12.50 cal/deg mol
C_p (gas)	8.52 cal/deg mol

Preparation

Potassium bromide is prepared by reacting bromine with potassium carbonate:

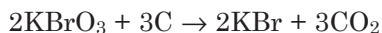


Potassium bromate, $KBrO_3$, is less soluble than the bromide. Thus, most potassium bromate may be removed by filtration. Remaining bromate can be converted to bromide by reduction with iron. After filtering iron from the solution, potassium bromide is obtained by evaporation and crystallization.

Another method of preparation involves treating bromine with warm concentrated aqueous solution of potassium hydroxide:



Bromide-bromate solution is evaporated to dryness. The residue is heated with charcoal:



Potassium bromide also can be prepared by treating iron turnings with a 35 wt% aqueous solution of bromine. The product ferrousferrous bromide is boiled in potassium carbonate solution containing a slight excess of 15% potassium carbonate (Dancy, W.B. 1980. Potassium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. p. 963. New York: Wiley Interscience). The method does not involve bromate formation. The second step of the process may be represented in the following reaction:



Potassium bromide also can be produced by electrolytic process.

Analysis

Elemental composition: K 32.85%, Br 67.15%. Potassium can be determined in solid form by flame testing. In aqueous solution, potassium can be measured by flame photometry, ICP/AES or electrode methods. Bromide ion can be analyzed in aqueous solution by ion chromatography.

Toxicity

Potassium bromide ingested in large doses can cause CNS depression. Other symptoms of chronic intake are mental deterioration and an acne-type skin eruption.

POTASSIUM CARBONATE

[584-08-7]

Formula: K_2CO_3 ; MW 138.21

Synonyms: potash; pearl ash; salt of tartar

Occurrence and Uses

Potassium carbonate occurs in wood ashes. It is one of the first known salts of potassium and was used historically in recovering metallic potassium. The compound has numerous potential applications. However, in most cases the cheaper and equivalent sodium carbonate is used. An important application of potassium carbonate involves making specialty television glass. Other applications are in pottery; soaps and liquid shampoos; process engraving and lithography; to depress the freezing point of water in fire extinguishers for unheated warehouses; and in tanning and leather work. An important use of this compound is preparing several other potassium salts.

Physical Properties

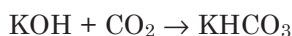
Colorless monoclinic crystals or granular powder; hygroscopic; density 2.428 g/cm³ at 20°C; melts at 891°C; decomposes on further heating; very soluble in water 112 g/100mL at 20°C and more soluble in boiling water, 156 g/100mL at 100°C; aqueous solution strongly alkaline; insoluble in alcohol and acetone.

Thermochemical Properties

ΔH_f°	-275.1 kcal/mol
ΔG_f°	-254.2 kcal/mol
S°	37.17 cal/deg mol
C_p	27.35 cal/deg mol

Preparation

Potassium carbonate is produced most conveniently by passing carbon dioxide into an aqueous solution of caustic potash, evaporating the solution to obtain the bicarbonate, and heating the bicarbonate:



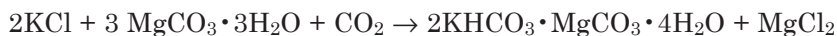
The carbonate salt also can be prepared by heating potassium formate in air or oxygen:



Potassium formate obtained from purified producer gas (see Potassium Formate) is heated in a rotary furnace having free access to air.

At ordinary temperatures, the carbonate salt crystallized from water is obtained as a dihydrate, $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$

The carbonate also can be made from potassium chloride, magnesium carbonate trihydrate and carbon dioxide under 30 atm at ordinary temperatures by Engel-Precht process:



The hydrated double salt on ignition decomposes giving potassium carbonate that may be extracted with water:



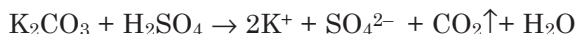
Small amounts of potassium carbonate were derived historically from leaching wood ash. The process is now obsolete.

Reactions

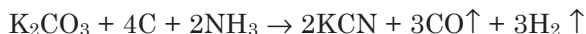
When carbon dioxide is passed into an aqueous solution of potassium carbonate, potassium bicarbonate is produced:



Reactions with dilute acids evolve carbon dioxide:



Potassium carbonate-carbon mixture reacts with ammonia at high temperatures to form potassium cyanide:



Analysis

Elemental composition: K 56.58%, C 8.69%, O 34.73%. The salt can be identified from its physical and chemical properties. Its aqueous solution is highly alkaline. Reaction with dilute acids evolves CO_2 with effervescence. The latter can be identified by GC-TCD or GC/MS. The primary characteristic mass ion for CO_2 is 44. Also, CO_3^{2-} anion can be measured by ion chromatography. Potassium can be analyzed by various instrumental and wet methods (see Potassium).